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BIMONTHLY REPORT NO. 4

ON THE

WATER-ACTIVATED BATTERY

Period:

28 March - 28 May 1960

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EXTENSION SAME  
REASON 3 d (3)

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PREFACE

The first three bimonthly reports covered the period 22 June - 21 December 1959. The funds on this project were depleted at the end of that period and work was halted during renegotiation. The contract extension did go into effect by the end of March 1960 and work was resumed without a change in purpose.

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## I. ABSTRACT

Following an extension of the contract, work has been resumed in April 1960 without any change in objectives. In preparation for phase 3 an attempt was made to simplify and improve the battery construction. It was discovered that tinned silver foil can be "spot-soldered" to magnesium without flux and that the use of this very simple type of bonding gives equally satisfactory battery performance. A successful run at an environmental temperature of +37°C, including peak current loads of 8 amperes, has been demonstrated.

## II. PURPOSE

### Phase 1:

To demonstrate the feasibility of a large model, chemically rechargeable, magnesium-silver chloride battery, activated by three per cent salt solution at room temperature and delivering an average current of 3 A at 12 V for at least 60 minutes. The voltage regulation at a maximum load current of 5.3 A shall equal or surpass the stability obtained previously.

### Phase 2:

To demonstrate reasonably satisfactory performance of this battery at environmental temperatures of -40°C and +40°C, using a variety of electrolytes such as three per cent salt solution, tap water and others. It is recognized, however, that such performance cannot be expected to match that at room temperature.

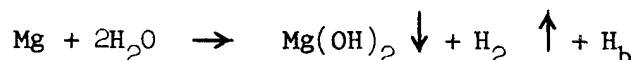
### Phase 3:

To fabricate and deliver six battery cases and 30 complete sets of chemical recharges for field testing purposes, including instructions on the proper handling, activation, deactivation, disposal and temperature control.

III. FACTUAL DATAA. Attempts to Reduce the Corrosion of the Magnesium Anode

Early in January of this year the results of a research and development program by another company indicated that the nature of the electrolyte in a water-activated battery may have an appreciable effect on the rate of corrosion of the magnesium anode in the cell. It was pointed out in the first bimonthly report that the rate of heat evolution is appreciable and is dependent on the corrosive action of magnesium. This heat evolution ( $H_b$ ) does not contribute to the discharge mechanism, although it is roughly proportional to it.

The reaction causing this heat evolution is shown below.



If this reaction could be eliminated or reduced appreciably, hydrogen formation would be reduced and with it heat evolution. Therefore several experiments were performed on small single-cell sample batteries to determine if the addition of additives to the electrolyte had any effect on the hydrogen formation, and thus heat generation.

Three different electrolytic solutions were used in these experiments. These are listed in Table I with their compositions.

TABLE I  
ELECTROLYTES USED IN CORROSION TESTS

Electrolyte	Composition with Respect to Water	Remarks
NaCl	3% by weight	Standard for test
$\text{CrO}_3$	0.5% by weight	Even at this small concentration it attacked the AgCl
$\text{Mg}(\text{ClO}_4)_2$	1 mol per liter	No Improvement

Several experiments were performed with each type of solution and with loads that would simulate those on the actual battery. At first a 2% solution of  $\text{CrO}_3$  was used and then a 1% solution; but in both cases serious ill effects were observed on the silver chloride cathode. This effect was still observed even with a 0.5% solution. It should be noted that the  $\text{CrO}_3$  decreased magnesium corrosion, but its use had to be abandoned because of its effect on  $\text{AgCl}$ . The electrolyte made from  $\text{Mg}(\text{ClO}_4)_2$  did not show any improvement over the standard  $\text{NaCl}$  electrolyte. All tests in this series of experiments were run at room temperature.

It has been concluded from this set of experiments that the magnesium corrosion problem cannot be alleviated easily by putting selected additives into the electrolyte. Therefore the design of the battery will continue according to previous plans because the heat generation problem still remains as an important factor.

#### B. Spot-Soldering Thin Silver to Magnesium Foil

The work done in this area during the reporting period is an improvement on the work described in Section V, A of the first bimonthly report. This previous report explained the technique that was developed to bond the silver to the magnesium with an epoxy resin. With this technique curing had to be accomplished at high temperature and high pressure. There are a number of drawbacks with this technique; for example:

1. The bonding between the magnesium and the silver, referring to both the resin adhesion and the quality of the spotwelds, was not very good, and more importantly,
2. The manufacturing technique with this procedure was complicated and time consuming, especially in the production of the large number of cells required by phase 3 of the contract.

When work was resumed on this contract it was decided to investigate this problem once again to try and simplify the manufacturing technique. The epoxy resin side of the problem was attacked first in the hopes of eliminating the high curing temperature aspect. If this curing problem could be eliminated then several layers could be stacked and processed in a press at one time instead of individually, and pilot plant production could be greatly increased.

Experiments were conducted using several different resins other than the original epoxy resin. Curing was accomplished in 15 minutes at 130°C; if curing were to be done at room temperature it could be expected to take 24 hours for a thin film. The only improvement with this resin was to reduce the curing temperature from 150° to 130°C. The second resin tried was , which is a butyral adhesive and does not require an activator. This resin was also cured at 130°C for 15 minutes. Thus no improvement was achieved against the second drawback mentioned above.

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The first drawback was then attacked. The weakest point in this problem of bonding the magnesium and silver was with the silver. At first it was thought that the magnesium was causing the problems. Experiments were then conducted with silver that was tarnished with a polysulfide and silver that was chromated. These two kinds of treated silver were used with the  resin and better adhesion was achieved. Through these experiments a new approach was found.

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Earlier experiments had shown that magnesium could be spot welded to the silver by means of a nichrome wire rolled down to 2 mil. The wire was then inserted as a small strip between the two metals, and spot welded. So it was decided to try and achieve good electrical contact between the magnesium and silver with the aid of an intermediate metal layer and without the aid of a resin.

Experiments along this approach began with putting a zinc or zinc and tin strike on the magnesium to give the electrical

resistance or low melting point that was needed for soldering. In conjunction with this coating of the magnesium, the silver was also tinned and attempts were made to spot weld or spot-solder the treated metals together. The tinning material was a paste solder called Hercules Swif (50-50 solder and flux) manufactured by the Hercules Chemical Company in New York City. This material had been used in other unrelated projects and found to be quite useful. The zinc surface adhered to the magnesium but it was porous. Further experiments showed that good spot-soldering could be achieved without the strikes on the magnesium and this striking step was eliminated.

The state of the art has indicated that spot welding pure magnesium and pure silver together is very difficult. Our experiments have shown that zinc coated magnesium can be bonded to untreated or tin-plated silver and good electrical contact is achieved. Tin-plated silver can also be bonded to pure magnesium to produce the same results. Our basic discovery in these experiments was that tinned silver could be spot soldered to the pure magnesium even without flux. This is in contradiction with known magnesium soldering technology.

The reason for this fact seems to be that the soldering process occurs very quickly leaving no time for an oxide layer to form on the magnesium surface. Magnesium is always covered with an oxide layer that must be broken up. In our process the welding is done very quickly and under pressure. This pressure undoubtedly breaks up the oxide and enables the solder to reach the magnesium. Thus a simple solution was obtained for the electrical contact problem.

We have ordered tin-cladded silver from the Texas Instrument Company, Metals and Controls Division, Brattleboro, Mass. Thus the same process can be used without having to coat the silver here at  This would speed up our pilot plant production.

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It was then decided to investigate and see if this new process would provide a bond that was both mechanically strong and sufficiently corrosion resistant. If this were not the case we could still use the  resin. Some small scale corrosion tests were therefore made to determine the necessity of the resin.

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In these experiments a 3% salt solution was heated to 75°-80°C and duplicate samples of five different cells were immersed in the bath. These cells had the following configurations:

1. Pure magnesium spot-soldered to tinned silver
2. Magnesium with a zinc strike spot-soldered to pure silver
3. Magnesium with a zinc strike spot-soldered to tinned silver
4. Magnesium with a zinc strike coated with pure resin spot-soldered to pure silver (the resin was supposed to fill in the porous zinc areas)
5. Magnesium with a zinc strike coated with pure resin spot-soldered to tinned silver.

We attempted to duplicate the actual operating conditions for the battery in these experiments but with appropriate scale factors taken into account. Thus the experiments began with the electrolyte at 40°C. The solution was then warmed to 85°C in one hour's time. The final temperature achieved was 82°C and had been at that level for the last 10 minutes of the run. All spot-solderings appeared to be in good condition. This experiment was run a second time but the solution then consisted of 3%-NaCl and 2-1/2% MgCl. This simulates the actual magnesium corrosion environment to be encountered in the full scale battery. In this experiment a higher starting temperature was used (the temperature after 15 minutes of operation was 60°C, after 30 minutes 75°C, after 45 minutes 85°C), and after the 60-minute run the temperature was 89°C. The spot welds of all

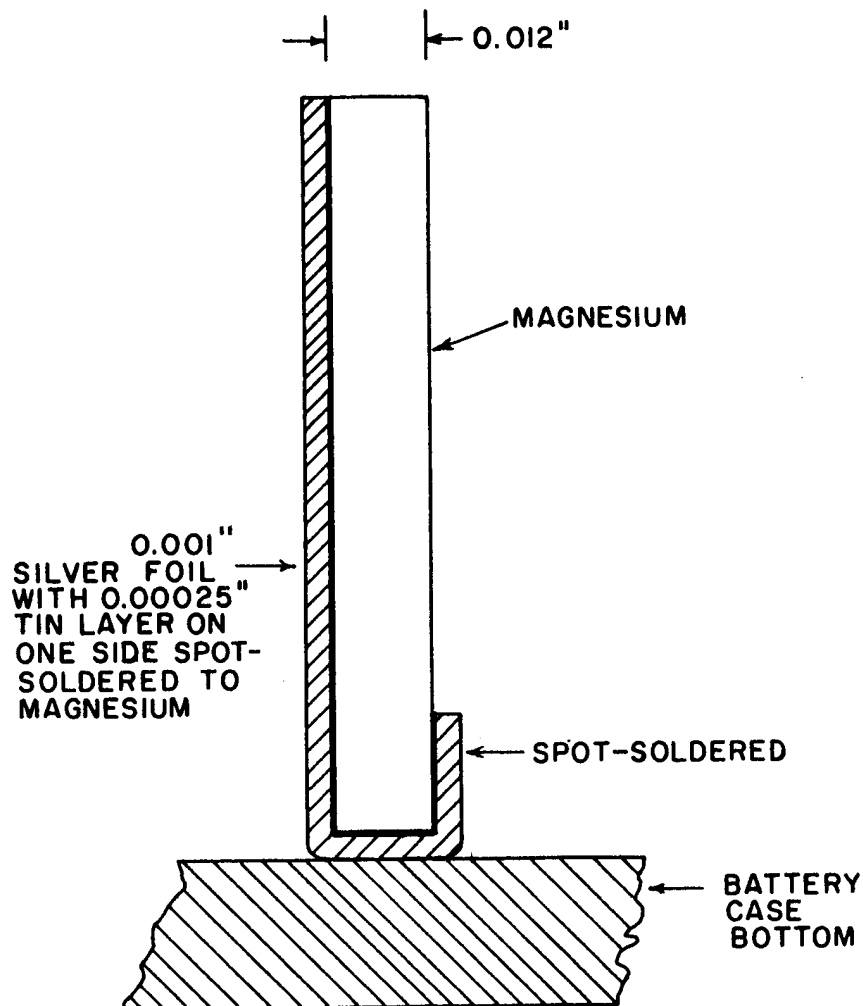
samples remained in very good condition. There was some magnesium corrosion but the electrical contact between the magnesium and the silver remained firm, so this approach will work very well in the final design.

Because of the excellent results achieved with these experiments it was decided to perform a small scale battery test using four cells of final size. Before this experiment was performed a slight modification was made in the cell structure, and this is shown in Figure 1. This modification consisted in wrapping the silver foil around the end of the magnesium and spot-soldering it on the back of the magnesium. This was done in an attempt to prevent to some extent intercell electrolyte leakage once operation of the battery was begun. In previous runs with the older bonding techniques, the silver foil just ran the length of the magnesium. This experiment proved that:

1. power output could be met,
2. the voltage and current could be maintained beyond the 60-minute requirement,
3. the spot welds between the silver and magnesium were still in good condition, and
4. the corrosion of the magnesium was at a reasonably low level.

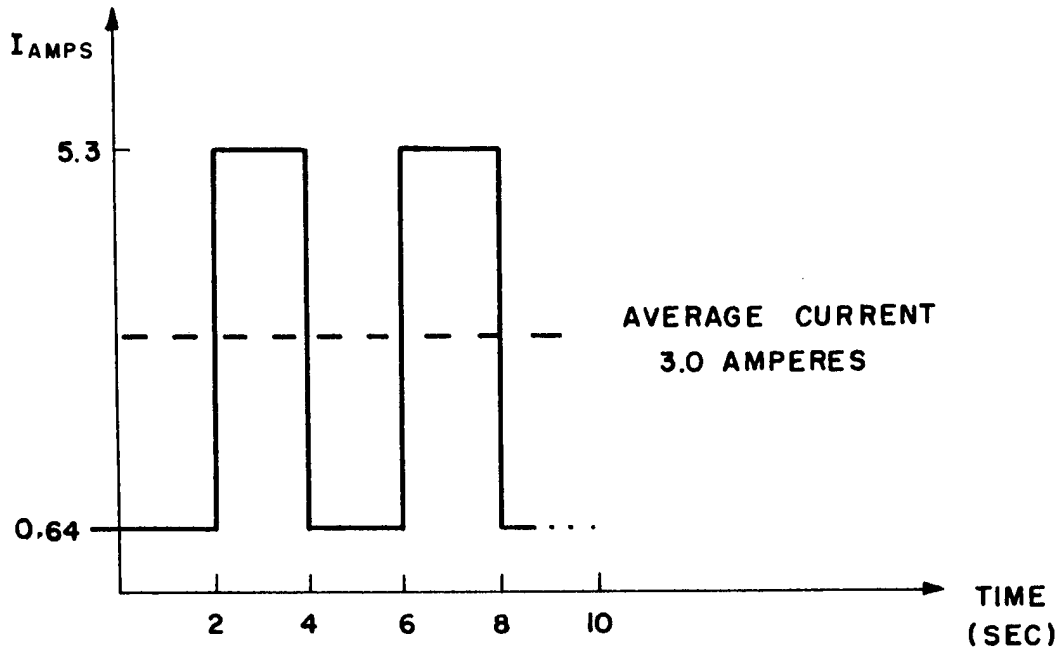
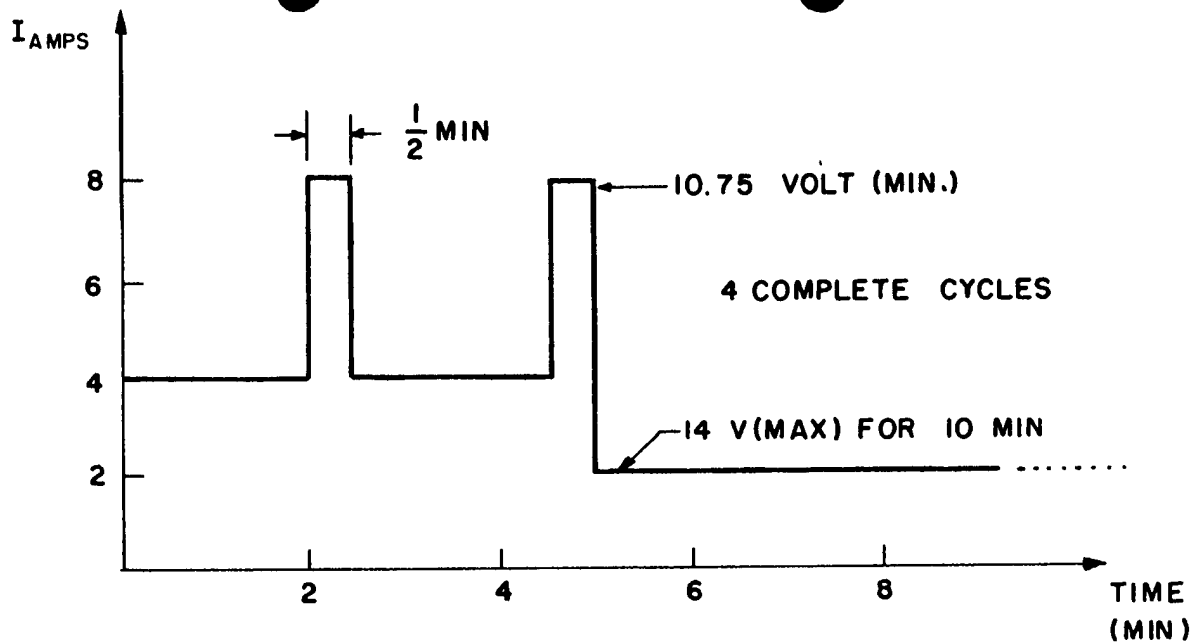
The standard load for tests of this sort, using four full-size cells, was described in the second bimonthly reports. On March 18, 1960 the customer visited  and indicated that he was interested in another type of loading. He wanted to know if the present battery design could sustain this new type of load. The requirements for this load are shown in Figure 2a; the load requirements called for by the contract are shown in Figure 2b. During the full scale test we tried to simulate this new type of loading, but we could not incorporate the eight desired 0.5-minute cycles of peak current because this would drain too much energy from the battery.

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CELL CONFIGURATION FOR FULL SCALE TEST OF THE NEW BONDING PROCESS

FIGURE 1



LOAD REQUIREMENT ON BATTERY  
FIGURE 2

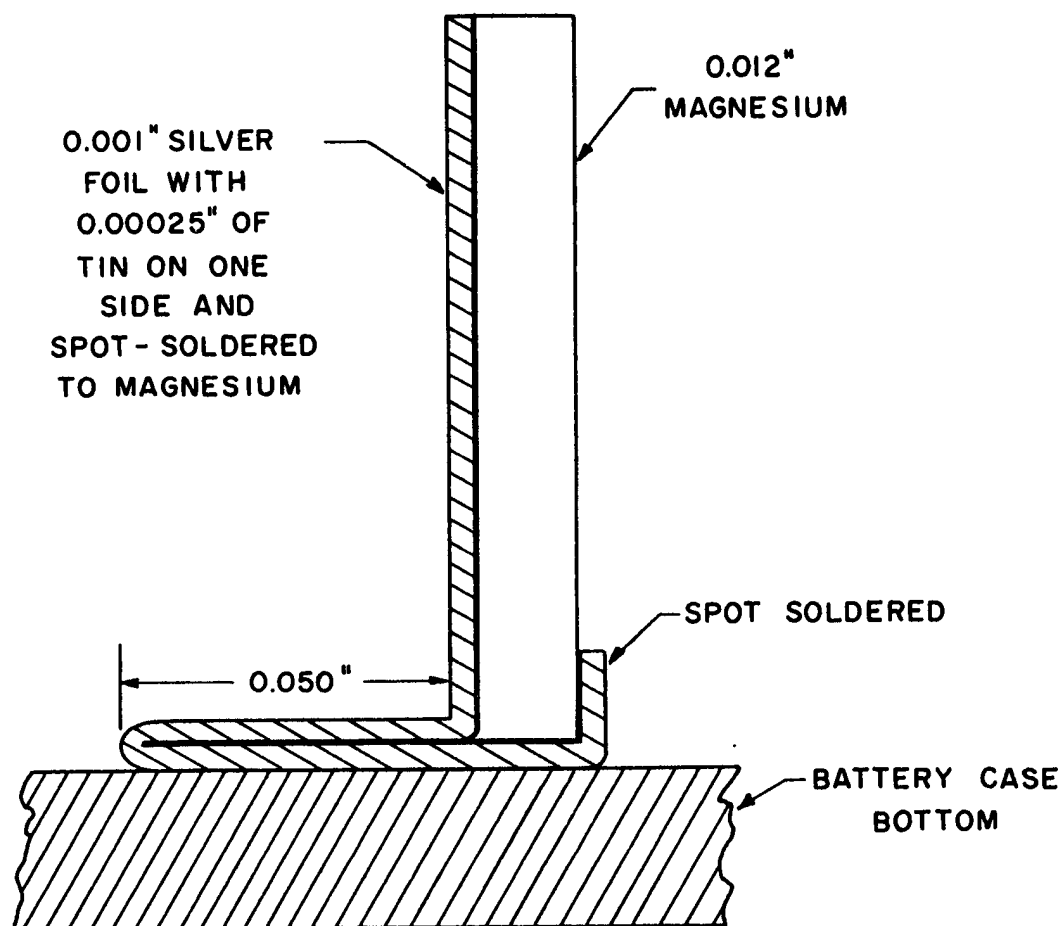
We could however determine if the 8-ampere peak could be obtained with the voltage limitations given; the voltage requirement is one of the most important features in this case. Thus this new load requirement was incorporated into the test just described.

The results from this experiment were rather surprising. At the normal current level of 5.3 amperes, the battery was delivering 6.0 volts. It should be noted that this was only a four cell test so the voltage was liberal and conservative as compared with a full nine cell battery. When a load of 8 amperes was applied to the battery for 30 seconds, the voltage was not any smaller than at the 5.3 ampere level. Normally as a result of the internal resistance of the battery, a lower voltage would have been expected. When the load level was returned to 5.3 amperes, the battery voltage was higher for some minutes than it had been prior to the imposing of the 8-ampere load. Thus it can be assumed that for the full scale battery the voltage would be in excess of the minimum 10.75 volts required by this new type of load. In this experiment the current surge tests were performed twice at about 20-minute intervals.

As a result of these experiments the following cell construction technique is now being used:

1. A tin layer is applied to the silver.
2. The tin layer and magnesium foil are cleaned.
3. The silver foil is spot-soldered to the magnesium foil by means of this tin layer.
4. The procedure is then the same as described in the second bimonthly report with some minor modifications.

Another feature to be incorporated in the battery construction is shown in Figure 3. It is hoped that this new construction will further reduce the internal leakage of the cell system. This leakage is caused by the fact that there is no clear-cut separation between the individual cells. The individual cell stacks fit rather



NEW SILVER FOIL SEAL CONSTRUCTION

FIGURE 3

loosely inside the battery case, and a certain amount of electrolyte contact between cells is still present. Spacers were originally inserted between the cells (see Bimonthly Report No. 2, page 7) but these have been eliminated to simplify fabrication and assembly, and thus a certain amount of leakage occurs. Our new technique for bonding the silver to magnesium enables us to correct this leakage without introducing additional components into the battery system and thereby reverting back to a complicated design. This new feature provides a 50-mil silver foil leakage seal around cell edges, and it should provide more battery capacity. With increased capacity the internal heat production is reduced, and cooling problems are not as great.

#### C. High Temperature Performance

High temperature performance was discussed rather thoroughly along with some experimental results in Bimonthly Report No. 3, Section III, C. The results were obtained without the use of a real battery.

During the present reporting period it was decided to rerun this same test, but this time an actual battery of new design would be used instead of an electric heater element. However, the sealing feature described in Figure 3 was not used in this test. It is believed that the seal will improve the high temperature performance quite a bit. A test will be made with the new type of seal at a later date. The cell configuration for this test was the same as that shown in Figure 1, and thus there was still some intercell leakage.

This high temperature test run was run under a high environmental temperature (37°C) and with a nine cell battery. The loading on the battery during this test also included four 8-ampere current surges for 15 seconds each. This 15-second surge period is sufficient to determine if the battery could meet the new load requirement. The full 30-second period for the surge was not used because the surge current in this test was superimposed on the battery's

contractually required load, and thus would have exerted an exceptionally heavy drain on the battery.

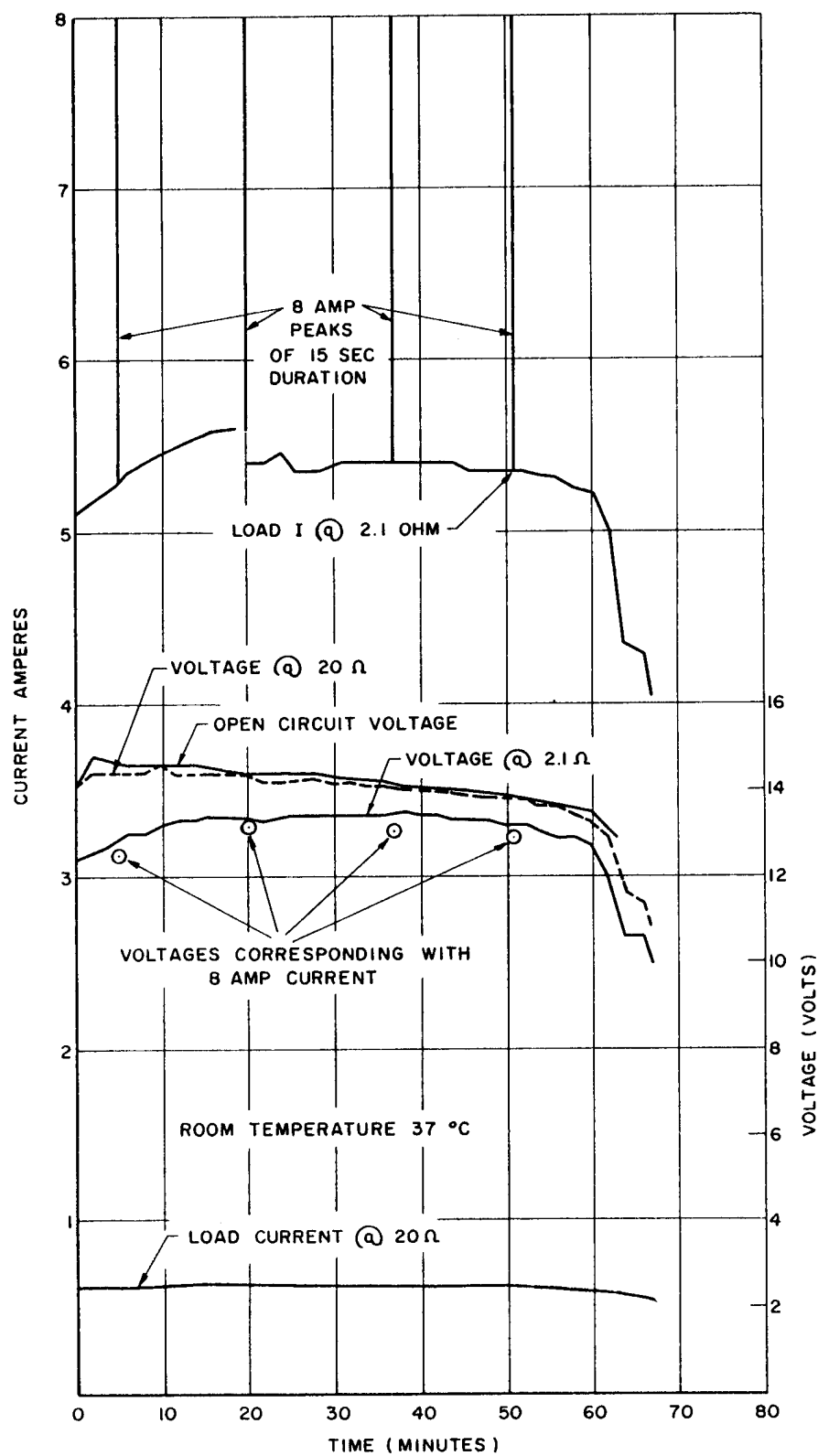
This test showed that the output voltages were very good, and for the 8-ampere surges the battery voltages were 12.5, 13.2, 13.1 and 12.9 volts respectively (they were all in excess of the 10.75 volt limit prescribed by the customer.) The test was a standard one except for the high environmental temperature and the 8-ampere surges. The relative humidity in the steam tunnel was 24%.

The 8-ampere test was performed in the following fashion. Under normal testing a timing switch would be putting out 2-second duration 5.3-ampere pulses every other two seconds as shown in Figure 2b. The operation of this switch was interrupted for the surge tests. During the interruption the load resistance was quickly changed to produce an 8-ampere pulse of 15-second duration.

The temperature of the battery during this test did run very close to the boiling point of the electrolyte in spite of the vaporization cooling. However the boiling of the battery was within reason and could be controlled. Salt water was added to the battery only once and that was only after 49 minutes of operation. Water was also added to the outside environment four times during the 60-minute run. The load curves obtained from this test are shown in Figure 4.

The foaming action of the battery (particularly at the 0.5 hour level) is still somewhat objectionable. During this test an anti-foaming agent (silicone) was added to the battery but it had no effect on the foaming action. An additive is still being sought that will suppress this undesirable foaming.

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HIGH TEMPERATURE LOAD TEST

FIGURE 4

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Attempts to reduce the rate of corrosion of the magnesium anode and the resultant heat evolution through additives to the electrolyte were unsuccessful. Although chromic acid appeared to reduce the corrosion rate it also adversely affected the silver chloride cathode. Magnesium perchlorate had no apparent effect.

A novel method for bonding a silver foil to magnesium foil has been developed. Tinned silver can be "spot-soldered" to magnesium without the use of any flux. This discovery simplifies and improves the battery construction with only a minor sacrifice in magnesium corrosion. It also permits the easy construction of a narrow silver-rim around the magnesium foil, which promises to reduce internal leakage and hence heat evolution.

Exploratory load tests on a new type of cycle, involving peak currents of 8-amperes for 30 seconds, were very successful. Terminal voltages at this peak load remained above 12 volts at room temperature or higher.

A high room temperature test run of a full-size battery using external vaporization cooling technique was successful.

Except for some minor changes in the design of the battery case and manufacturing technique, Phase 3 can now be initiated.

**V. FUTURE PLANS**

The main task during the next period will be the fabrication and delivery of batteries as described in Section II, Phase 3.

**VI. PERSONNEL**

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